

Modeling the Effect of Water Activity and Storage Temperature on Chemical Stability of Coffee Brews

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This work was addressed to study the chemical stability of coffee brew derivatives as a function of water activity (a_w) and storage temperature. To this purpose, coffee brew was freeze-dried, equilibrated at increasing a_w values, and stored for up to 10 months at different temperatures from -30 to 60 °C. The chemical stability of the samples was assessed by measuring H_3O^+ formation during storage. Independently of storage temperature, the rate of H_3O^+ formation was considerably low only when a_w was reduced below 0.5 (94% w/w). Beyond this critical boundary, the rate increased, reaching a maximum value at ca. 0.8 a_w (78% w/w). Further hydration up to the a_w of the freshly prepared beverage significantly increased chemical stability. It was suggested that mechanisms other than lactones' hydrolysis, probably related to nonenzymatic browning pathways, could contribute to the observed increase in acidity during coffee staling. The temperature dependence of H_3O^+ formation was well-described by the Arrhenius equation in the entire a_w range considered. However, a_w affected the apparent activation energy and frequency factor. These effects were described by simple equations that were used to set up a modified Arrhenius equation. This model was validated by comparing experimental values, not used to generate the model, with those estimated by the model itself. The model allowed efficient prediction of the chemical stability of coffee derivatives on the basis of only the a_w value and storage temperature.

KEYWORDS: Modeling; coffee; pH; acidity; Arrhenius equation; staling

INTRODUCTION

In the past decade, coffee brew derivatives have encountered increasing success in eastern countries where coffee drinking represents an almost new habit. On the other hand, in countries with a long coffee-drinking tradition, the popularity of these products is still hindered because of their poor quality, mostly attributable to their very low chemical stability. Quality depletion, which starts immediately just after brewing, is characterized by a change in the flavor profile and an increase in perceived sourness (1–4). These changes are accompanied by a pH decrease, corresponding to an increase in titrable acidity, whose clear explanation is not put forward at present.

It is well-known that a great amount of acids and their derivatives is generated during roasting from carbohydrate precursors via nonenzymatic browning pathways (5–8). Despite a major fraction of roasted coffee, acidity can be attributed to the formation of formic, acetic, glycolic, and lactic acids from sucrose (9, 10); significant amounts of quinic acid esters and lactones are also generated from degradation of chlorogenic acids during roasting (11). The increase in quinic acid upon hydrolysis of these esters and lactones has been considered the main driving factor responsible for acidity development in the brew (12–17). Further observations, indicating that oxygen is

not involved in the reactions responsible for pH decrease, seemed to confirm the hypothesis. Actually, it was shown that the content of quinic acid lactone decreased significantly upon heating of a coffee brew, while the content of the relevant acid increased by nearly the same amount (18, 19). However, according to van der Stegen and van Duijn (12), the increase in quinic acid would account for only 25% of the overall acidity developed. In addition, it was also found that a significant amount of acid precursors was not water soluble (9). With regard to the esters of acids other than quinic acid, the formation of monoesters in the presence of carbohydrates was also suggested (20). In this case, the pH decrease would be the consequence of complex reactions, probably related to nonenzymatic browning pathways, involving carbohydrates and acids rather than a simple hydrolysis of the esters. In light of these findings, there is much circumstantial evidence that mechanisms, other than hydrolysis of quinic acid lactones, could contribute to the observed increase in acidity during coffee staling.

Nowadays, coffee brews are processed to obtain a number of products, which are usually stored in a wide temperature range, with different a_w values. Considering both hydrolysis and nonenzymatic browning to be involved in their quality depletion during storage, water content and hence a_w are expected to play a key role in determining the rate of pH decrease. In addition, the effect of a_w is likely to be strongly affected by storage temperature. However, because of the uncertainty and complex-

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Table 1. Solid Concentration of Coffee Samples Equilibrated at Increasing a_w

a_w	solid concentration (% w/w)
0.01	100.00
0.33	97.04
0.52	93.70
0.84	77.98
0.99	15.00
0.99	1.8

ity of the chemical reactions concerned, the effect of a_w and storage temperature on the rate of acidity development can be difficult to figure. Undoubtedly, these results would be of great interest to find out processing and storage conditions, allowing one to obtain more chemically stable coffee brew derivatives. In addition, the knowledge of the a_w and temperature dependence of coffee brew stability is strictly necessary to develop shelf-life models that are able to predict coffee derivative stability in times that are consistent with their short life span in competitive markets.

In light of these considerations, the aim of the present paper was to model the combined effect of a_w and storage temperature on the stability of a possible coffee matrix, taken as an example. To this purpose, coffee brew was freeze-dried and equilibrated at increasing a_w values from 0.01 to 0.99. In this way, samples representative of different coffee brew derivatives (freeze-dried coffee, concentrated coffee brews with different solid fractions, and ready-to-drink coffee beverages) were obtained from the same coffee matrix. The rates of H_3O^+ formation during storage for up to 10 months at different temperatures in the range from -30 to 60 °C were measured. Data were elaborated to find a reliable model able to predict coffee derivative stability in a wide range of conditions. Following the approach of previous papers carried out to obtain predictive models of the stability of different food matrices (21–25), this research was also addressed by evaluating the usefulness of the Arrhenius equation and studying the effect of a_w on its parameters. The predictive model achieved represents a useful mathematical instrument to assist in shelf-life decisions relevant to coffee brew and its concentrated derivatives.

MATERIALS AND METHODS

Sample Preparation. Ground dark-roasted coffee was purchased at a local market. Coffee beverage was obtained by extraction of 100 g of coffee powder with 1 L of distilled water at 90 °C (Kenwood aromatica CM720, New lane, Havant, England). After extraction, the coffee beverage was quickly cooled at room temperature in an ice-cooled bath.

The coffee extract was freeze-dried (Mini Fast model 1700, Edwards Alto Vuoto Spa, Milano, Italy) and equilibrated at different a_w values to obtain samples with different solid weight fractions. In particular, 10 cm diameter Petri dishes containing approximately 5 g of freeze-dried coffee were placed in vacuum desiccators containing saturated salt solutions having equilibrium relative humidity (ERH %) values up to 100% and were maintained at 25 °C. The salts, with relevant ERH % values in brackets, were used as follows: P_2O_5 (1%), LiCl (12%), $MgCl_2$ (33%), MgN_2O_6 (52%), NaCl (74%), $CdCl_2$ (82%), and K_2O_4S (97%) (Carlo Erba, Milano, Italy). Samples with $a_w = 0.99$ were equilibrated over distilled water. Preliminary trials were carried out to determine the lengths of time necessary to hydrate samples at the desired a_w , which was less than 4 h. Samples with decreasing coffee solid concentrations were thus obtained (Table 1).

Coffee samples with different a_w values were introduced in glass vials, hermetically sealed with butyl septa and metallic caps, and stored in the dark at -30 , -18 , -7 , 0 , 10 , 20 , 30 , 45 , and 60 °C for up to 10

months. At increasing lengths of time during storage, samples were removed from thermostated cells and rehydrated by adding the amount of distilled water required to reach a solid concentration of 1.8% (w/w). Preliminary trials showed that freeze-drying and rehydration had no significant effect ($p > 0.05$) on the pH of the beverage.

Total Solid Content. The total solid content was determined according to the AOAC (26).

Water Activity. The water activity (a_w) was determined by means of a dew-point measuring instrument (Aqua Lab, Decagon, Pullman, WA) at 25 °C.

Calorimetric Analysis. Calorimetric analyses were made by means of a TA 4000 differential scanning calorimeter (Mettler Toledo, Greifensee, Switzerland) equipped with a DSC 30 low-temperature measuring cell and a TC11 TA processor and connected to a Graph Ware software (TA 72.2/5, Switzerland). The heat flow was calibrated using indium (heat of fusion, 28.45 J/g). The temperature was calibrated with *n*-butyl alcohol (mp, -89.5 °C), water (mp, 0 °C), and indium (mp, 156.6 °C). Coffee samples were exactly weighed and placed in 40 μ L capacity aluminum pans. An empty aluminum pan was used as a reference. Samples were heated from -120 to 300 °C at 10 °C min^{-1} . Thermograms were analyzed for the onset temperature of ice melting.

pH. The pH of coffee beverages was assessed by a Mettler Toledo 355 pH meter (Lou Analyzer, Halstead, Essex, England). The H_3O^+ concentration was calculated according to pH definition.

H_3O^+ Formation Rate (k). The changes in H_3O^+ concentration were observed to follow the zero-order kinetic, and relevant rates (k) were calculated by linear regression of H_3O^+ concentration as a function of storage time. The effect of temperature on k was evaluated by means of the Arrhenius equation (27):

$$k = k_o \times e^{-E_a/RT} \quad (1)$$

where k is the reaction rate constant, R is the molar gas constant (8.31 J/K/mol), T is the absolute temperature (K), E_a is the activation energy (J/mol), and k_o is the frequency factor. To better estimate the apparent activation energy (E_a) and frequency factor (k_o), the following reparametrized Arrhenius equation was used

$$k = k_{ref} e^{-E_a/R[(1/T)-(1/T_{ref})]} \quad (2)$$

where k_{ref} is the apparent oxidation rate at T_{ref} (28, 29). T_{ref} was chosen as 288 K, which is the central value of the temperature interval considered in the study. The apparent activation energy E_a and k_{ref} were determined by linear regression analysis and used to calculate k_o :

$$k_o = e^{[\ln k_{ref} + (E_a/RT_{ref})]} \quad (3)$$

Data Analysis. The results reported in this work are the average of at least two determinations carried out on different samples, and the coefficients of variation, calculated as the percentage ratio between the standard deviation and the mean value, were less than 5% for total solid content, a_w , temperature of ice melting, and pH and less than 10% for k .

The significance of the differences among means was determined using the Tukey–Kramer test (JMP, ver. 3.2.5, SAS Institute, Cary, NC). Means were considered to be significantly different at $p < 0.05$. Least-squares linear regression analysis was performed by using Statistica for Windows (ver. 5.1, Statsoft Inc., Tulsa, OK, 1997). Best-fitting analysis was performed by using Table Curve 2D for Windows (ver. 4, SPPs Inc., Chicago, IL).

RESULTS AND DISCUSSION

Coffee samples with different a_w were stored for increasing time in the temperature range from -30 to 60 °C and assessed for pH. The changes in pH of coffee with 0.99 a_w , corresponding to 1.8% (w/w) solid concentration, are shown, as examples, in Figure 1. A clear decrease in pH, whose intensity was proportional to storage temperature, was observed, confirming that coffee staling is associated with an increase in hydrogen

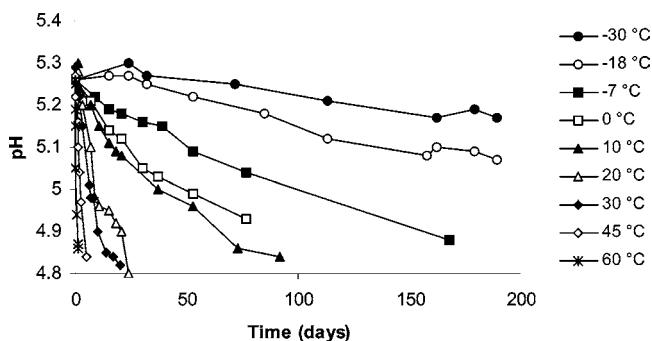


Figure 1. pH of coffee with 0.99 a_w , corresponding to 1.8% (w/w) solid concentration, as a function of storage time at different temperatures.

ion concentration (1–3, 12–17). pH data were thus used to calculate the changes in H_3O^+ concentration during storage of coffee samples (Figure 2). Apparent rate constants of H_3O^+ formation (k , $M\ day^{-1}$) were calculated by linear regression analysis according to the zero-order equation.

Similarly, the values of k ($R^2 > 0.90$, $p < 10^{-2}$) relevant to coffee with increasing a_w and stored in the temperature range from 60 to $-30\ ^\circ C$ were calculated. Figure 3 shows the effect of a_w on the H_3O^+ formation rate of coffee samples stored at different temperatures.

By analyzing the evolution of k (Figure 3), it can be observed that at ca. 0.8 a_w , corresponding to a solid content of 78% (w/w), the H_3O^+ formation rate presented a maximum value, whose intensity increased with temperature. This result appears to be of considerable interest since it clearly indicates that drying does not allow the stability of coffee to be obtained, unless very low a_w values are reached. In fact, drying to intermediate moisture levels promotes an unexpectedly fast quality depletion, which proceeds at rates considerably higher than those observed in the freshly brewed coffee (a_w 0.99, 1.8 w/w solid concentration). Only when a_w is lower than ca. 0.5, which corresponds to a solid content of about 94% (w/w), the development of acidity is comparable or lower than that of the diluted beverage stored at the same temperature. Such an a_w value can thus be hypothesized to be a critical boundary beyond which quality depletion of coffee brew derivatives should be expected to quickly proceed. Consequently, intermediate a_w values, typical of most food ingredients that contain concentrated coffee brew, are associated with the highest quality depletion rate.

It is noteworthy that the a_w dependence of the reaction rate tends to a bell-shape curve with a maximum at intermediate a_w values when food solids chemically react with each other in an aqueous system (30, 31). This is the well-known case of reactions, such as nonenzymatic browning, whose reactant mobility is kinetically hindered at low a_w values. Upon further a_w increases, molecules quickly react due to water plasticization but the enhancement in reaction rate is progressively counterbalanced by reactant dilution. Overcoming a critical a_w , generally set at intermediate values, the dilution effect prevails over the plasticization one, so that a maximum rate is identified.

Results shown in Figure 3 seem to contradict the hypothesis that the decrease in pH observed during coffee beverage staling is solely attributable to hydrolysis of esters and lactones previously formed during roasting (12–18). In fact, in this case, water should be regarded as a reactant rather than as a diluting media. Consequently, upon hydration, the H_3O^+ formation rate should progressively enhance even beyond $a_w = 0.8$, which was clearly not observed (Figure 3). For this reason, the presence of a maximum rate at intermediate a_w suggests reactions other than hydrolysis contribute to coffee beverage staling. It can be

inferred that solids contained in the coffee beverage could undergo nonenzymatic browning reactions following mechanisms that are the proceedings of those observed during roasting. Reactants for nonenzymatic browning are actually still present even in dark-roasted coffee beans. In other words, browning reactions are not completed during roasting but only temporarily blocked by the decreased mobility of the coffee matrix, which underwent glass transition upon roasting. Although roasted coffee beans are known to be vitreous at room temperature with a T_g around $170\ ^\circ C$ (32), the structures of the freeze-dried coffee extracts considered in this study were well below glass transition in the entire a_w range. In fact, calorimetric analysis indicated coffee samples to have the physical state of a solution in most temperature and a_w conditions considered. Only in diluted samples stored at -30 and $-18\ ^\circ C$, water partially froze and reactants were concentrated in the unfreeze solution (Table 2). This result is consistent with the relatively low molecular weight of melanoidins as compared to other polymers (33, 34).

It is thus reasonable that, in adequate a_w conditions, such as those that characterize coffee beverages, extracted melanoidins could continue to react during storage, determining the formation of acid compounds. This hypothesis is supported by the fact that coffee acids have been reported to beget high amounts of monoesters in the presence of carbohydrates, leading to the pH decrease of the brew as a consequence of complex reactions, probably related to nonenzymatic browning pathways (20). In addition, a major fraction of coffee acidity is well-known to be generated on roasting from carbohydrate precursors (5–9). Their possible formation even during coffee beverage storage is probably not negligible. On the basis of these considerations, it can be inferred that the formation of acids upon nonenzymatic browning could contribute, together with the hydrolysis of esters already present in the coffee extract, to the pH decrease during storage of the beverage.

As regards the effect of temperature on H_3O^+ formation rate, Figure 3 shows that coffee samples stored at 45 and $60\ ^\circ C$ presented a progressive increase in k with a_w . By contrast, below $45\ ^\circ C$, no significant changes in k were observed up to a_w 0.52. When such a a_w value was overcome, a sudden increase in k was detected (Figure 3, inset). These results confirm that the effect of a_w of coffee staling is strongly dependent on storage temperature. To further investigate the critical effect of temperature, k values were plotted according to the Arrhenius model (Figure 4).

An Arrhenius type relation between H_3O^+ formation rate and temperature was clearly achieved in samples equilibrated at a_w values higher than 0.52 in the entire temperature range considered. In particular, contrary to what was observed in other food products (21, 23, 24), no deviations from linearity were observed in samples undergoing freeze concentration (Table 2), suggesting that the Arrhenius equation was a proper predictive model of quality depletion during coffee brew derivative storage. At lower a_w values, k was described by the Arrhenius model only in samples stored at temperatures higher than 0 – $20\ ^\circ C$. Below this temperature, k resulted in considerably lower than expected values on the basis of the Arrhenius equation. These very low k values were not reported in Figure 4 because they were out of scale, but they clearly indicated that, independent of storage temperature, the system was particularly stable from a chemical viewpoint. It is likely that although the system is not vitreous due to the low molecular weight of the extracted compounds, it exerts a peculiar stability as a consequence of its low a_w . In other words, water would be enough to make the system amorphous but not to allow solute reactivity.

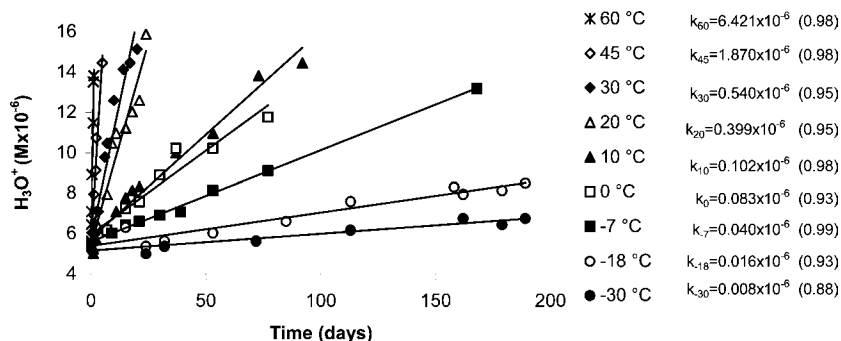


Figure 2. H_3O^+ concentration of coffee with 0.99 a_w as a function of storage time at different temperatures. The apparent zero-order rate constants of H_3O^+ formation (k , M day^{-1}) and the relevant determination coefficients (in brackets) are also shown.

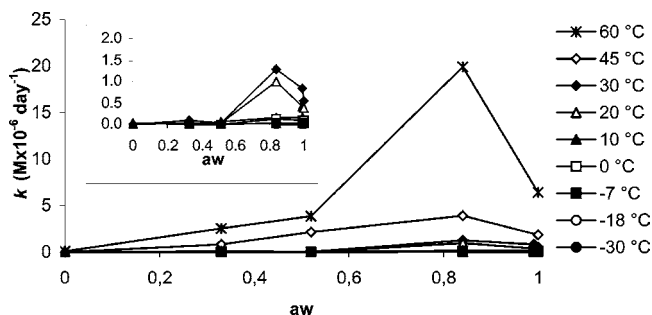


Figure 3. Apparent zero-order rate constants of H_3O^+ formation as a function of a_w of coffee samples stored at different temperatures. In the inset: Detail of data in the k range from 0 to $2 \text{ M} \times 10^{-6} \text{ day}^{-1}$.

Table 2. Temperature of Ice Melting of Coffee Samples with Different a_w

a_w	temperature of ice melting ($^{\circ}\text{C}$)
0.01	ND ^a
0.33	ND
0.52	ND
0.84	-31.16
0.99	-26.97
0.99	-9.27

^a ND, not detectable.

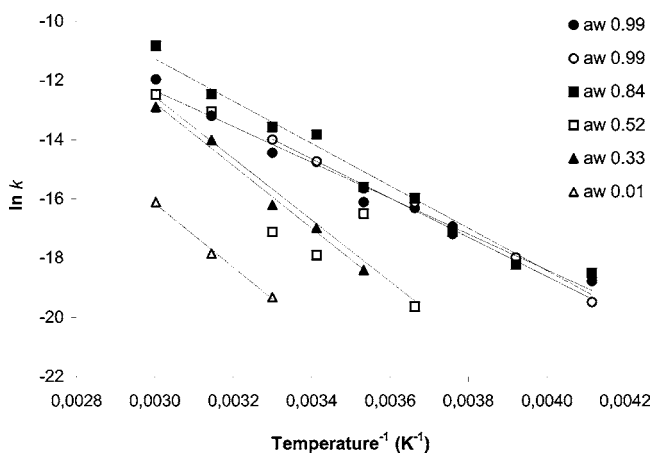


Figure 4. Apparent zero-order rate constants of H_3O^+ formation, expressed as $\ln k$ ($\text{M} \times 10^{-6} \text{ day}^{-1}$), as a function of storage temperature of coffee with different a_w . Lines were obtained by regression analysis according to eq 1.

In light of these data, it could be suggested that the predictive efficiency of the Arrhenius equation is maintained as long as k values higher than ca. $0.002 \times 10^{-6} \text{ M day}^{-1}$ ($\ln k = -20$) are concerned. Below this value, which is, however, very low, H_3O^+

Table 3. Apparent Activation Energy (E_a) and Frequency Factor (k_0) as a Function of Coffee a_w ^a

a_w	E_a (kJ/mol)	k_0	R^2	SE
0.01	89.5	1.0×10^7	0.99	0.167
0.33	87.7	1.6×10^8	0.99	0.244
0.52	86.6	1.3×10^8	0.83	1.301
0.84	59.4	2.6×10^4	0.97	0.466
0.99	55.2	2.7×10^3	0.99	0.167
0.99	50.4	3.5×10^2	0.98	0.302

^a Statistical parameters of regression according to reparameterized eq 2 are also reported.

formation proceeds at rates much lower than those predicted by the Arrhenius equation. In these conditions, the use of the Arrhenius equation to predict quality depletion would lead to an overestimation.

Regression analysis of k as a function of temperature was performed for each coffee concentration according to reparameterized Arrhenius eq 2 (T_{ref} equal to 288 K) (Figure 4). Parameters of regression were used to calculate the apparent activation energy (E_a) and frequency factor (k_0) for each coffee a_w (Table 3).

The water activity was found to affect the temperature sensitivity of coffee, changing both the apparent activation energy and the frequency factor in the Arrhenius equation (35, 36). In particular, the apparent activation energy was observed to progressively decrease as a_w increased. By contrast, k_0 initially increased with the increase in a_w but decreased on further hydration so that a maximum value was identified at 0.33 a_w . These results indicate that the reactions leading to H_3O^+ formation became less sensible to temperature changes as a_w increased and that the number of successful collisions between reactants was higher in concentrated systems. These results are in agreement with data shown in Figure 3 and suggest that the reaction rate tends to a maximum value at $a_w = 0.8$ by virtue of the lower activation energy despite the fact that the number of collisions is not optimal. In other words, at low a_w , the number of collisions between reactants is very high but the reaction proceeds slowly because only a limited part of the molecules has enough energy to make the reaction occur (37). At a_w around 0.8, because of the high molecular mobility, the number of collisions is expected to be lower but most of them possess the energy required for quick rearrangement and product formation. Finally, in diluted systems, the reaction rate decreases because collisions, despite energetic, rarely occur. These results confirm that water does not behave as a reactant but, more properly, as a diluting media, supporting the hypothesis that not only hydrolytic reactions are involved in H_3O^+ formation during coffee staling.

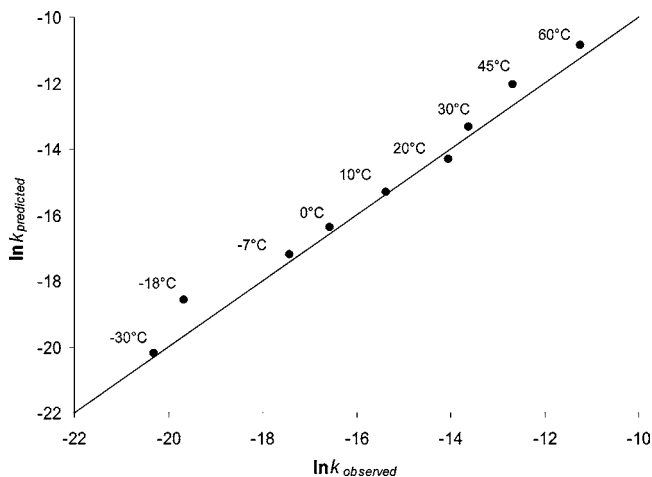


Figure 5. Apparent zero-order rate constants of H_3O^+ formation, expressed as $\ln k$ ($[\text{H}_3\text{O}^+] \text{ day}^{-1}$), predicted by eq 6 as a function of experimental data for coffee with 0.74 a_w stored at different temperature.

Best-fitting analysis allowed us to identify simple descriptive equations of E_a and k_o as a function of coffee a_w . E_a data (kJ/mol) were well-described ($R^2 = 0.96$, $p < 10^{-4}$, $\text{SE} = 3.94$) by the following simple equation:

$$E_a = a + ba_w^2 \quad (4)$$

where a and b are regression coefficients equal to 92.201 and -40.653 , respectively.

k_o was accurately described ($R^2 = 0.99$, $p < 10^{-7}$, $\text{SE} = 5974660$) by the Gaussian equation:

$$k_o = c \times e^{[-0.5(a_w - d/f)^2]} \quad (5)$$

where c , d , and f are regression coefficients equal to 1.779×10^8 , 0.401, and 0.159, respectively.

Substituting eqs 4 and 5 in eq 3, a general model for H_3O^+ formation rate in coffee can be achieved as follows:

$$k = c \times e^{[-0.5(a_w - d/f)^2]} \times e^{-(a + ba_w^2)/RT} \quad (6)$$

It can be observed that the only independent variables in eq 6 are temperature and water activity. For this reason, it actually represents a model able to predict H_3O^+ formation rate in coffee brew derivatives on the basis of their a_w values and storage temperature.

The predictive efficiency of this model was verified by applying a widely recognized methodology based on comparison of experimental values of k , not used to generate the model, with those estimated by the model itself (24, 38). In particular, coffee samples with 0.74 a_w were prepared and stored in the temperatures range from 60 to -30 °C. H_3O^+ formation rates were thus experimentally determined and compared to those predicted by eq 6. For the 0.74 a_w coffee sample, eq 6 predicted E_a and k_o equal to 69.9 kJ/mol and 1.8×10^6 , respectively. The comparison of experimental and predicted k values is presented in Figure 5. In particular, values predicted substituting a_w and temperature in the model (eq 6) were plotted on log scales against the observed values. It can be observed that the points obtained this way are on the line of equivalence, indicating that the model proposed is able to accurately predict apparent H_3O^+ formation rate of coffee on the basis of only its a_w and storage temperature. However, it must be observed that proper application of the model is strictly dependent on the availability of a

reasonable acceptance limit chosen on the basis of accurate sensory data.

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